Poly[(methyl methacrylate)-*co*-(methacrylic acid)] Microgel Particles: Swelling Control Using pH, Cononsolvency, and Osmotic Deswelling

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ABSTRACT: The swelling of poly[(methyl methacrylate)-*co*-(methacrylic acid)] (PMA-MAA) microgel particles (prepared using 17 mol % MAA) dispersed in water can be controlled by pH adjustment, addition of alkanols, and addition of water soluble homopolymer. Transmission electron microscopy revealed two-dimensional order for PMA-MAA particles deposited on a grid from alkaline solution. The swelling of the microgel particles was studied by means of photon correlation spectroscopy. The stability of the particles was investigated using turbidity−wavelength measurements; flocculation occurred when the pH was less than 6. A buffer ($NaHCO_3$/NaOH) was employed to stabilize the pH of the PMA-MAA dispersions at about pH = 10. The hydrodynamic diameter of the PMA-MAA particles is sensitive to pH with a maximum at about pH = 8. PMA-MAA microgel particles deswell upon addition of an alcohol (methanol or 2-propanol) or poly(ethylene glycol) (PEG). Poly(*N*-isopropylacrylamide) (PNP) microgel particles also deswell in aqueous alcohol solutions. Re-entrant swelling was observed for PMA-MAA and PNP particles when the volume fraction of alcohol exceeded 0.4. The swelling behavior of PMA-MAA and PNP in water−alcohol solvents is attributed to cononsolvency effects. Incompatibility of PEG and PMA-MAA is suggested as the most likely cause for the osmotic deswelling observed upon addition of PMA-MAA particles to aqueous PEG solution. Comparison of the swelling properties of PMA-MAA to those of PNP and literature data suggests that PMA-MAA microgel particles behave as weakly charged networks. Moreover, the comparison reveals that microgel particles and *macrogels* exhibit important differences in swelling behavior.

Introduction

Whereas *macrogels* in general have dimensions greater than 1 mm, enabling their swelling properties to be investigated by optical microscopy,[1−5] *microgel* particles on the other hand have colloidal dimensions.[6−10] Microgel particles may be viewed as cross-linked latex particles which are swollen by a good solvent; colloidal stability results primarily from matching of the Hamaker constants of the swollen particles and solvent. Microgels are used in the surface-coatings industry to provide rheological control for high-solids formulations;[11] however, dissolved polymers and cosolvents may also be present. A question of fundamental and practical importance relates to how linear polymers and added solvents influence microgel particle swelling. The present work addresses these issues through a study of the swelling of poly[(methyl methacrylate)-*co*-(methacrylic acid)] (PMA-MAA) microgel particles in the presence of added alkanol and a linear homopolymer.

As microgel particles are several orders of magnitude smaller than macrogels, the former possess a much larger interfacial area and the ability to flow (in the dispersed phase). Microgels and macrogels are prepared using different methods. Macrogels may be synthesized at 4 °C using quiescent solutions in the presence of an accelerator.[5] The products tend to be homogeneous with respect to composition. Microgel particles are usually prepared at elevated temperature using rapidly stirred solutions in order to obtain stable, monodisperse particles. Particle growth involves oligomer formation, nucleation, and limited aggregation.[12] Subsequent growth occurs by addition of oligomers from the continuous phase to the particle surface. If the continuous phase contains a number of chemically distinct monomers (with different reactivity ratios), it is likely that the particles will contain a nonuniform distribution of these species.

The swelling of a neutral polymer network (microgel particle or macrogel) immersed in a good solvent is due to a balance of osmotic and elastic forces (F_o and F_{el}, respectively). Ionic networks have an additional osmotic contribution to the swelling (F_i) due to the higher concentration of mobile (nonassociated) ions within the network as a consequence of the Donnan equilibrium which is set up.[13] Therefore, the addition of fixed charged species to a network increases its swelling. The contribution of electrostatic repulsion between the fixed charged species to swelling may be neglected for weakly charged networks. Addition of excluded, free polymer (i.e., nonadsorbing polymer that is excluded from the network interior) to the continuous phase introduces another term (F_p). At equilibrium:

$$F_i + F_o = F_p + F_{el} \tag{1}$$

The free polymer decreases the net osmotic force acting across the network−solvent interface causing deswelling. Detailed theoretical models for the swelling of polyelectrolyte gels have been proposed.[14,15]

The pH dependence of the swelling of poly[(ethyl acrylate)-*co*-MAA] and poly[(methyl methacrylate)-*co*-(acrylic acid)] microgel particles has been reported by Rodriquez et al.[16] and Sawai et al.[17] swelling increased with increasing extents of neutralization. The swelling properties of ionic macrogels based on PMA-MAA[18] and poly[(*N*-isopropylacrylamide)-*co*-(acrylic acid)][5] have been studied as a function of pH and solvent composition. The former work showed that buffer accelerates the rate of swelling, while the latter system exhibited discontinuous volume transitions.

Poly(*N*-isopropylacrylamide) (PNP) microgel particles usually contain very low levels of ionic species, and

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Table 1. Molecular Weight Data for PEG Polymers

polymer	M_w[a]	M_w/M_n
PEG 0.2K	230	1.2
PEG 1.0K	1040	1.13
PEG 2.0K	1860	1.12
PEG 3.0K	3265	1.15
PEG 8.0K	8090	1.08
PEG 12K	11 800	1.10
PEG 15K	14 900	2.15
PEG 17K	16 900	1.80

[a] Weight average molecular weight (g/mol).

swelling is controlled primarily by polymer−solvent interactions. (The ionic species originate from the initiator and normally reside within the surface region.) In this work, we compare the swelling behavior of PMA-MAA and PNP microgel particles in an effort to assess the relative importance of ionic effects and polymer−solvent interactions to PMA-MAA particle swelling. Zhu and Napper[19] recently found continuous deswelling and re-entrant swelling in polystyrene-PNP core-shell particles dispersed in water−alcohol solutions. The deswelling of the PNP shell was attributed to cononsolvency due to clathrate structure formation. PNP macrogels exhibit discontinuous volume phase transitions when immersed in similar solutions.[4]

Deswelling of macrogels by addition of free, linear polymer (osmotic deswelling) has been widely studied.[20−23] We have studied the influence of added free polymers on the swelling of microgel particles.[24,25] Osmotic deswelling was observed in the PNP/water/PEG (PEG = poly(ethylene glycol))[24] and free polystyrene/ethylbenzene/polystyrene microgel systems.[25] In the latter work, comparisons with a thermodynamic model based on Flory's theory of network swelling were made.[25]

Experimental Section

Materials. Methyl methacrylate (MMA; Aldrich, 99%) and methacrylic acid (MAA; Aldrich, 99%) were purified by vacuum distillation prior to use. Ethylene glycol dimethacrylate (EGDM; Aldrich, 98%), *N*-isopropylacrylamide (NP; Kodak Eastman), *N*,*N*′-methylenebis(acrylamide) (BA; Aldrich, 99%), and ammonium persulfate (Aldrich, 98%) were all used as received. Water was Milli-Q grade. Methanol (MeOH; Tennants), 2-propanol (PrOH; May and Baker, AR grade), and ethylene glycol (EG; Fisons, 99%) were used as received. The PEG polymers (Koch-Light and Fluka) were analyzed using gel permeation chromotography (see Table 1) by RAPRA (U.K.).

Microgel Synthesis. PMA-MAA and PNP microgels were synthesized using "surfactant-free" emulsion polymerization. The PMA-MAA microgel (containing about 17 mol % MAA) was prepared using a seed-feed method. MMA (11.58 g, 0.116 mol), MAA (2.10 g, 0.0244 mol), and EGDM (0.35 g, 1.77 mM) were mixed, and 1.75 g of the solution was added to a 1 L, five-necked, round-bottom flask (rbf) containing deoxygenated water (600 mL). The rbf was immersed in an oil bath maintained at 80 ± 1 °C. A solution containing $K_2HPO_4 \cdot 3H_2O$ (0.25 g, 1.1 mmol) and ammonium persulfate (0.118 g, 0.517 mol), dissolved in 25 mL of water, was added to the rbf and the polymerization allowed to proceed for 40 min. The remaining monomer solution was added at a uniform rate over 90 min and the reaction allowed to proceed for a total of 16 h. The latex was purified by six centrifugation cycles using water and a further five cycles using aqueous $NaHCO_3$ (0.0412 M)/NaOH (0.0176 M) buffer (pH = 10). The microgel was stored at 5 °C. Samples used for transmission electron microscopy (TEM) and pH-dependent studies were centrifuged a further three times using dilute NaOH solution (pH = 10).

PNP microgel was prepared using a batch method. NP (4.2 g, 0.0371 mol) and BA (0.42 g, 2.72 mmol) were added to water (300 mL) maintained at 70 ± 1 °C in a three-necked, 1 L rbf. A solution of ammonium persulfate (0.21 g, 0.92 mmol) in 7 mL of water was added to the stirred solution under anaerobic conditions. The reaction was allowed to proceed for 16 h. The microgel was purified by 10 centrifugation cycles using water.

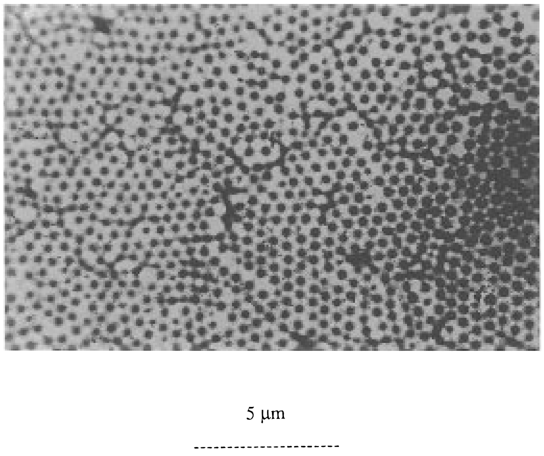

Figure 1. Transmission electron micrograph of PMA-MAA particles. The particles were dispersed in dilute NaOH solution (pH = 10) prior to deposition on the TEM grid.

Physical Measurements. Particle size measurements were performed using an Hitachi HS7S TEM instrument which was calibrated with a diffraction grating. Optical spectra were recorded over the range 400−620 nm using a Perkin Elmer Lambda 5 spectrophotometer. PCS data were obtained using a Brookhaven Zeta Plus instrument. The dispersions used for the pH study were allowed to equilibrate for 2 days (at a given pH) prior to the PCS measurements. The remaining PCS studies of PMA-MAA microgel particles were conducted using buffered $NaHCO_3$/NaOH solutions (see above); measurements were usually made within 2 h of addition of buffered dispersion. The PNP systems were investigated using buffered solutions. Measurements of the hydrodynamic diameter (d) were subject to a coefficient of variation of approximately 5%. We express the swelling in terms of the deswelling ratio: $\alpha = (d/d_o)^3$, where d_o is the value for the control at 25 °C. All PCS measurements were made at 25 °C. The PMA-MAA and PNP microgel concentrations were 0.050 and 0.025 wt %, respectively. The viscosities and refractive indices of the mixed solvents were obtained from the literature,[26] while those of the PEG solutions were measured at 25 °C using a calibrated Cannon-Fenske U-type capillary viscometer and an Abbé refractometer, respectively.

Results and Discussion

pH-Dependent Swelling of PMA-MAA. A representative transmission electron micrograph of PMA-MAA particles deposited from alkaline solution appears in Figure 1. The average particle size is 310 nm (standard deviation = 57 nm). The micrograph reveals extensive two-dimensional ordering. The particles are forced (by surface tension effects) to occupy a close-packed arrangement during solvent evaporation. Deswelling (through solvent loss) yields an ordered array of spaced particles. Such two-dimensional order has been reported previously for PNP microgel particles deposited from water.[6,24]

Representative hydrodynamic diameters of isolated particles can only be obtained by PCS in the absence of flocculation; otherwise, artificially high values are found. Long et al.[27] have shown that flocculation in latexes may be detected using optical density (OD)−wavelength (λ) measurements. The gradient of the $\log_{10}$(OD) versus $\log_{10}(\lambda)$ plot yields a parameter, n ($= -\mathrm{d}\log_{10}(\mathrm{OD})/\mathrm{d}\log_{10}(\lambda)$), which is very sensitive to particle aggregation. An abrupt decrease in the magnitude of n is indicative of

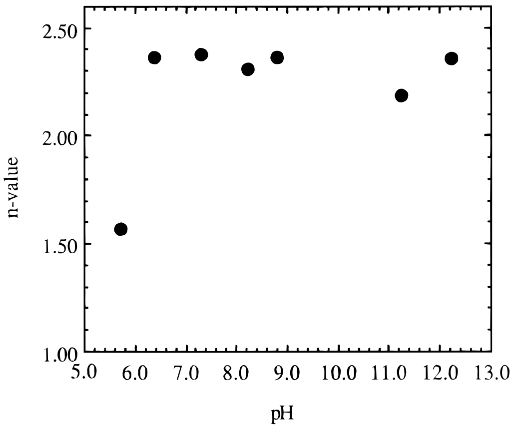

Figure 2. Influence of dispersion pH on the *n*-value (see text) of PMA-MAA.

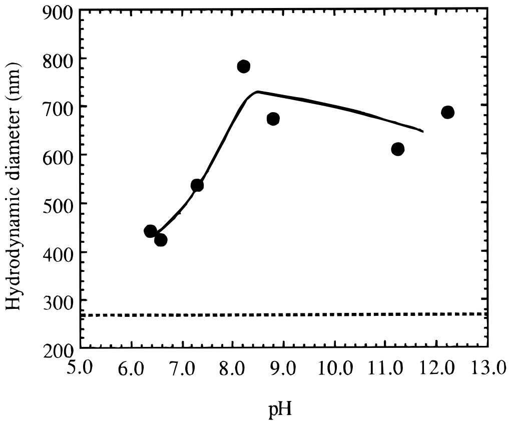

Figure 3. Variation of PMA-MAA hydrodynamic diameter with dispersion pH. The solid curve is a guide for the eye. The broken lines show the diameter of fully collapsed PMA-MAA.

flocculation.[27,28] Figure 2 shows the effect of dispersion pH on the *n*-value of PMA-MAA. The initial dispersion pH was 10. pH values lower and higher than 10 were obtained by addition of HCl and NaOH, respectively. (These dispersion pH values showed a tendency to drift during equilibration, e.g., the pH = 10 sample had a final pH of 8.8.) The data shown in Figure 2 reveal that the PMA-MAA particles are stable at pH values greater than 6. Flocculation at low pH is attributable to a significant difference between the Hamaker constants of the particles and solvent (due to particle deswelling) and decreased electrostatic stabilization (through neutralization of COO^-). That such effects are reversible was verified by the observation that addition of NaOH to a sample that had flocculated (changing the pH from 4 to 12) and gentle agitation caused redispersion.

Figure 3 shows the variation of the PMA-MAA hydrodynamic diameter with dispersion pH. These data are qualitatively similar to those obtained using poly[acrylamide-*co*-(acrylic acid)] macrogels[29] and poly[MAA-*co*-(acrylic acid)] microgels.[17] However, PMA-MAA microgel particles exhibit a more gradual swelling transition in the pH range 6–8 and a smaller swelling ratio at pH = 9 than reported for the macrogel. The pK_a of poly(MAA)[30] is 5.5. Therefore, the carboxylic acid groups are essentially fully ionizied[3] at pH = 8.0. Donnan equilbrium ensures that the concentration of mobile ions within the microgel particles is greater than that in the continuous phase. In the absence of added acid or base the ionic component of the osmotic force (F_i) is at a maximum and so is particle swelling. The COO^- groups are neutralized by the addition of HCl (proceeding from the particle surface to the interior) which causes deswelling through decreases in electrostatic repulsion and mobile ion concentration within the particles. Thus, the hydrodynamic diameter of PMA-MAA microgel particles tends to decrease with addition of HCl.

Addition of NaOH increases the concentration of sodium ions which decreases the difference between the concentration of mobile ions within the particle interior and the continuous phase (decreasing F_i). Increased screening of the charged species also occurs. These effects combine to decrease the swelling. The data shown in Figure 3 for pH values greater than 8 are in broad agreement with this explanation.

Siegel[2] has reported that pH-responsive macrogels only fully deswell if efficient ion transport is maintained throughout pH-induced deswelling. It is evident from Figures 2 and 3 that flocculation occurred prior to complete collapse of the PMA-MAA particles. It is not clear whether the PMA-MAA particles collapse fully at pH values lower than 6. We note that vitrification and a lack of pH buffering would not favor complete particle collapse.

The data shown in Figure 3 highlight the importance of pH control in experiments designed to assess swelling changes of PMA-MAA microgel particles. The problems associated with maintaining stable pH in alkaline solutions without the use of buffers are well known.[31] We opted, therefore, for pH control via a $NaHCO_3$/NaOH buffer system with a reported[32] pH of 10.0. In general agreement with Chou et al.[18] (who studied PMA-MAA macrogels), we found that the use of pH buffer greatly increased the rate of swelling of collapsed particles to their final equilibrium state. The data of Chou et al. for PMA-MAA macrogels immersed in buffer solutions (pH = 9) suggest that swelling equilibrium requires periods of the order of days.[18] However, we found that collapsed PMA-MAA microgel particles reached 75% of their equilibrium swelling volume within 8 min of addition to $NaHCO_3$/NaOH buffer. Equilibrium swelling was achieved within 3 h. Thus, the swelling transition for PMA-MAA microgel particles is much more rapid than that exhibited by the macrogel.

The continuous phase had a significant ionic strength (ca. 0.06 M) due to the electrolyte species of the buffer. The average hydrodynamic diameter of PMA-MAA particles in the buffered dispersion was 615 nm, which is similar to the value measured in the absence of buffer at pH = 11.2 (Figure 3).

Swelling of PMA-MAA and PNP Microgels in Water–Alkanol Mixtures. Polymer–solvent interactions may be investigated using solvent mixtures.[19] Figures 4 and 5 show the deswelling ratios of PMA-MAA and PNP microgel particles dispersed in a range of MeOH–water and PrOH–water solutions. The deswelling ratio decreases and passes through a minimum with increasing volume fraction of alcohol (ϕ_a) in each system. Re-entrant swelling occurs when ϕ_a exceeds 0.4. The volume fractions of alcohol required to produce the minimum deswelling ratio (ϕ_a*) and the trends in the data are comparable to those reported for related systems[19,33] (see Table 2).

It can be seen from Table 2 that the value of ϕ_a* is lower for the PrOH–water mixtures. In addition ϕ_a* occurs in the water-rich region. A cononsolvency mechanism based on clathrate structure[34] formation has been invoked to explain similar data.[19,33] (Cononsolvency refers to the phenomenon whereby the solubility of a

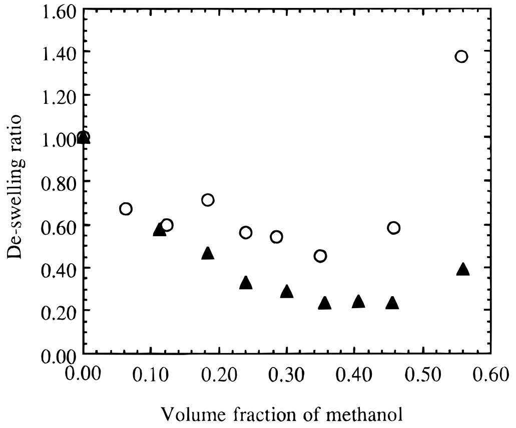

Figure 4. Deswelling ratios of PMA-MAA (○) and PNP (▲) in mixtures of MeOH and water.

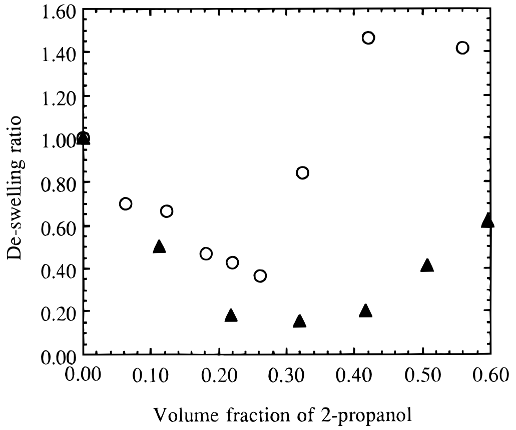

Figure 5. Deswelling ratios of PMA-MAA (○) and PNP (▲) in mixtures of PrOH and water.

Table 2. Mixed Solvent Compositions for Optimum Deswelling of PMA-MAA and PNP Microgel Particles

		ϕ_a* [a]			
polymer	system	MeOH	PrOH	temp (°C)	ref
PMA-MAA	microgel	0.38 ± 0.04	0.26 ± 0.02	25	*b*
PNP	microgel	0.42 ± 0.06	0.32 ± 0.06	25	*b*
PNP	core-shell particles	0.43	0.28	20	19
PNP	macrogel	0.30		25	33

[a] Volume fraction of alcohol at minimum deswelling ratio. [b] This work.

solute in a solvent mixture is worse than that of the solute in each of the pure solvents.) Water molecules are believed to encapsulate alcohol molecules in water-rich mixtures due to local ordering of the water structure (clathrate structure). The proportion of clathrate structure increases with ϕ_a (up to a critical value, ϕ_a^c) causing "dehydration" of the polymer. Attractive (hydrophobic) interactions between network polymer segments become dominant favoring deswelling. When $\phi_a > \phi_a^c$ encapsulation begins to fail and hydrophobic solvation effects become dominant. The value of ϕ_a^c for alcohol−water mixtures generally decreases with increasing size of the alkyl moiety.[33]

Polymer−solvent interactions are also important in network swelling. PNP macrogel preferentially adsorbs MeOH and ethanol from aqueous alcohol solutions.[33,35] In addition, poly(vinyl methyl ether) chains do not undergo the coil-to-globule transition in aqueous alcohol solutions with identical compositions to those that induced the transition for PNP.[36] Interactions between the polymer (P) and local solvent mixture (M) influence network swelling via a composition-dependent interaction parameter, χ_{PM}. Presumably, the cononsolvency phenomenon dominates the swelling behavior when χ_{PM} is above a critical value.

Comparison of the PNP and PMA-MAA swelling data (Figures 4 and 5) shows that PMA-MAA particles are more swollen at ϕ_a*, exhibit sharper deswelling transitions, and swell to a greater extent when ϕ_a exceeds 0.4. The first two observations are in agreement with swelling data obtained by Amiya et al.[3] for poly[NP-*co*-(acrylic acid)] macrogels containing low levels (<2 mol %) of acrylic acid in MeOH−water solutions. They found that macrogels containing more than 3 mol % acrylic acid did not deswell. (Fixed ionic groups resist deswelling and induce re-entrant swelling at lower alcohol volume fractions (cf. PNP).) In the present work the PMA-MAA microgel particles were prepared using 17 mol % MAA. Therefore, the swelling data appear consistent with a weak effective ionization within the particles. This conclusion must remain tentative due to structural differences between PMA-MAA and PNP. It was noted above that the buffer is a source of electrolyte which would tend to reduce internal electrostatic repulsion within the PMA-MAA particles through charge screening.

The increased extent of re-entrant swelling of PMA-MAA compared to PNP (see Figures 4 and 5) may be associated with *cosolvency*. Cowie et al.[37] have reported that MMA has increased solubility in mixtures of alcohol and water. The region of solubility moves to lower ϕ_a values with increasing alkyl chain size.

It is interesting to compare swelling data for microgel particles and macrogels composed of the same polymer. Hirotsu et al.[4] examined the swelling of PNP macrogels in aqueous MeOH solutions and observed discontinuous deswelling at 26 °C when $\phi_a \cong 0.18$. A similar transition is not apparent for PNP microgel particles (see Figure 4); the deswelling is gradual and continuous. In addition, our PNP microgel particles show a reduced tendency for deswelling in aqueous MeOH solution. The continuous nature of the PNP particle deswelling is probably due to a nonuniform cross-link distribution within the microgel particles.

Deswelling of PMA-MAA Microgels in Aqueous Solutions of PEG. Addition of free polymers to microgel dispersions is another method for controlling the swelling of microgel particles.[24,25] We initially selected poly(acrylic acid) as the free polymer as it was postulated that Donnan exclusion would result in osmotic deswelling. However, the PMA-MAA microgel particles flocculated in the presence of neutralized poly(acrylic acid) which prevented a detailed PCS study. It is thought that the decreased electrostatic repulsion between particles (due to charge screening) allows depletion flocculation to occur. Therefore, an electrically neutral polymer, PEG, was employed as the free polymer. The stability of the PEG/PMA-MAA mixtures was investigated by turbidity−wavelength measurements for a range of PEG molecular weights (Table 1). The results appear in Figure 6. The *n*-values are all above 2.0, indicating isolated particles. The *n*-values obtained for the other PMA-MAA/PEG systems examined (not shown) were also consistent with stable dispersions.

In using PCS to measure particle size from a dispersion containing dissolved linear polymer, we have made three assumptions. Firstly, we assume that the microviscosity encountered by the microgel particles is the

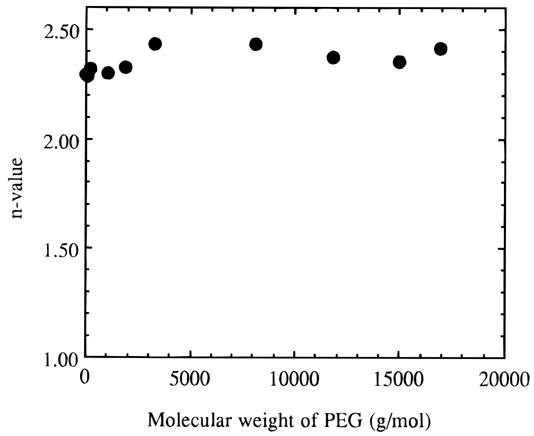

Figure 6. Variation of the *n*-value of PMA-MAA with molecular weight of added PEG (volume fraction of PEG = 0.13).

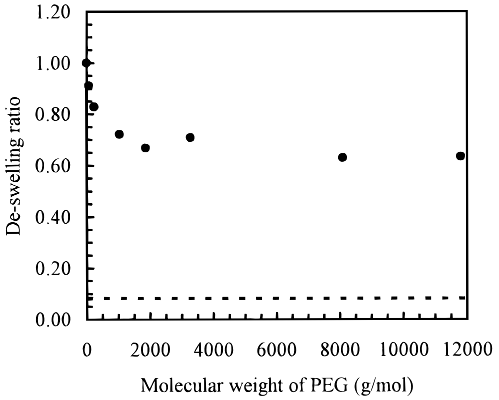

Figure 7. Deswelling ratio of PMA-MAA microgel particles as a function of molecular weight of added PEG ($\phi_F = 0.13$). The broken line is the deswelling ratio for fully collapsed PMA-MAA particles.

same as the measured macroviscosity. It is unlikely that microgel particles slip past the free polymer in the systems investigated. It is also assumed that adsorption of PEG onto the PMA-MAA microgel particles does not occur. Complex formation between poly(acrylic acid) and poly(ethylene oxide) may occur at low pH.[38] However, the pH was fixed at about 10 for the PMA-MAA/PEG systems which would not favor such association. The final assumption is that the proportion of light scattered from the PEG solutions is insignificant. It was found that only PEG solutions containing PEG 15K and PEG 17K scattered light significantly; the scattered intensity increased with increasing PEG concentration. The ratio of scattered intensity from PMA-MAA microgel particles to that from the corresponding PEG solution (scattering ratio) was used to accept or reject PCS data. The data presented below were obtained using PMA-MAA/PEG/water dispersions where the scattering ratio was ≥20.

Figure 7 shows the variation of α with PEG molecular weight at fixed volume fraction of free PEG ($\phi_F = 0.13$). A sharp decrease in α occurs as the PEG molecular weight approaches about 230 g/mol. Above this value, a small decrease of α which tends toward a limiting value is evident. These data differ from those reported for the PNP microgel/PEG system where a substantial decrease in α occurred when the PEG molecular weight exceeded 1450 g/mol.[24] Penetration of the microgel particle interior by free polymer may occur if the radius of gyration of the free polymer chains is smaller than the pore size of the microgel particle. In the present work it is assumed that the free polymers studied are small enough to penetrate the PMA-MAA microgel particle interior. However, we have no direct evidence to support this assumption.

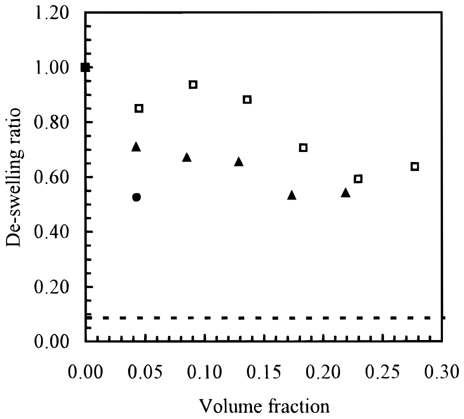

Figure 8. Effect of the volume fraction of EG (□), PEG 8K (▲), and PEG 17K (●) on the deswelling ratio of PMA-MAA microgel particles. The broken line is the deswelling ratio for fully collapsed PMA-MAA particles.

The influence of EG and PEG concentration on α is shown in Figure 8. These data reveal that EG reduces the solvent quality for PMA-MAA. (It was found that α decreased in a linear manner with volume fraction of EG up to $\phi = 0.6$.) PEG 8K and PEG 17K induce significant deswelling of PMA-MAA particles when $\phi_F = 0.05$, and further deswelling probably occurs at higher ϕ_F.

The data obtained using EG suggest PEG-PMA-MAA incompatibility as the cause of the PEG-induced deswelling of PMA-MAA microgel particles. (The interaction between PEG and PMA-MAA is therefore repulsive, with a positive value for the network polymer−free polymer interaction parameter, i.e., $\chi_{PF} > 0$.) These data may be compared to swelling data obtained for polystyrene macrogel in the presence of incompatible linear polymer (PMMA).[39] Momii et al.[39] found that increasing the molecular weight of PMMA enhanced deswelling of the macrogel. The data shown in Figure 7 show a similar trend until the PEG molecular weight reaches ca. 2K. Thereafter, the swelling behavior is different as the swelling is little influenced by PEG molecular weight. The PMA-MAA microgel particles display a reduced tendency toward osmotic deswelling compared to the system of Momii et al.

PEG migration into the microgel particle interior is not thermodynamically favorable (although limited penetration may occur). Any exclusion of PEG produces an osmotic force which induces deswelling (i.e., $F_p > 0$ in eq 1). However, F_i opposes deswelling. This would contribute to the relative lack of deswelling of PMA-MAA compared to polystyrene[39] macrogel and PNP microgel systems.[24] It seems unlikely that complete collapse of PMA-MAA microgel particles could be achieved through PEG addition; at some limiting value electrostatic repulsion and osmotic pressure due to mobile ions would prevent further deswelling. Moreover, PCS measurements would become unreliable in such highly viscous dispersions.

Theoretical results for swelling of polyelectrolyte macrogels in the presence of incompatible free polymer[14] show that the critical ϕ_F necessary to produce (discontinuous) deswelling moves to lower values with decreasing ionic charge of the network. Comparison with the present data (Figure 8) suggests that PMA-MAA particles behave as weakly ionic microgels when dispersed in PEG/buffer solution.

Conclusions

The data presented above represent the first systematic study of the effects of solvent composition and added free polymer on the swelling of ionic microgel particles. We have shown that swelling of PMA-MAA microgel particles can be controlled using three methods: pH variation, cononsolvency, and addition of linear polymer. pH variation produced the greatest absolute change in hydrodynamic diameter. However, the data obtained using alkanols and PEG showed significant deswelling. pH buffers (primarily intended for pH control) appeared to affect the PMA-MAA microgel particles so that the swelling properties were those expected of a weakly ionic network. Comparison with PNP microgel showed that solvency effects strongly determine the swelling behavior of PMA-MAA particles.

The data obtained in this study (when combined with our earlier work[24,25]) lead to the conclusion that microgel particles possess qualitatively similar swelling properties as macrogels of similar composition. However, comparison of the swelling properties of microgels and macrogels reveals several important differences: (1) Swelling transitions exhibited by microgel particles occur in a continuous manner, whereas those reported for macrogels are abrupt (sometimes discontinuous). (2) The deswelling ratios measured for our microgels in the presence of alkanols or added free polymer are greater (i.e., less deswelling) than those reported for macrogels. (3) Microgel particles swell (and deswell[24]) more rapidly than macrogels of similar composition. The differences in the swelling behavior of microgels noted above are attributed to compositional variations within the particles (e.g., nonuniform cross-link distribution) and their colloidal dimensions.

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